

# Calculating the Diffusive Flux of Persistent Organic Pollutants between Sediments and the Water Column on the Palos Verdes Shelf Superfund Site Using Polymeric Passive Samplers

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## S Supporting Information

**ABSTRACT:** Passive samplers were deployed to the seafloor at a marine Superfund site on the Palos Verdes Shelf, California, USA, and used to determine water concentrations of persistent organic pollutants (POPs) in the surface sediments and near-bottom water. A model of Fickian diffusion across a thin water boundary layer at the sediment-water interface was used to calculate flux of contaminants due to molecular diffusion. Concentrations at four stations were used to calculate the flux of DDE, DDD, DDMU, and selected PCB congeners from sediments to the water column. Three passive sampling materials were compared: PE strips, POM strips, and SPME fibers. Performance reference compounds (PRCs) were used with PE and POM to correct for incomplete equilibration, and the resulting POP concentrations, determined by each material, agreed within 1 order of magnitude. SPME fibers, without PRC corrections, produced values that were generally much lower (1 to 2 orders of magnitude) than those measured using PE and POM, indicating that SPME may not have been fully equilibrated with waters being sampled. In addition, diffusive fluxes measured using PE strips at stations outside of a pilot remedial sand cap area were similar to those measured at a station inside the capped area: 240 to 260 ng cm<sup>-2</sup> y<sup>-1</sup> for *p,p'*-DDE. The largest diffusive fluxes of POPs were calculated at station 8C, the site where the highest sediment concentrations have been measured in the past, 1100 ng cm<sup>-2</sup> y<sup>-1</sup> for *p,p'*-DDE.



## INTRODUCTION

Much of the Palos Verdes Shelf (PVS) Superfund site, off of the coast of California, USA, is under more than 50 m of water. The water column and sediments at the site are contaminated with persistent organic pollutants (POPs), including dichlorodiphenyltrichloroethane (DDT), its breakdown products (e.g., dichlorodiphenyldichloroethylene (DDE), dichlorodiphenyldichloroethane (DDD), and 1-chloro-4-[2-chloro-1-(4-chlorophenyl)benzene (DDMU)), and polychlorinated biphenyls (PCBs).<sup>1–6</sup> These contaminants are the legacy of industrial wastes produced throughout the mid-20th century and released through the wastewater outfall of the Joint Water Pollution Control Plant, operated by the Los Angeles County Sanitation Districts (LACSD).<sup>7</sup> Like other sites where industrial sources of environmental contamination have been controlled or eliminated, the sediments, originally a sink for contaminants, have become a continuing source of contamination to the water column.<sup>8–12</sup>

The flux of POPs between the sediment bed and water column may occur through many different mechanisms.<sup>13</sup> Compounds may desorb from sediment solids to the water column during resuspension events or as benthic organisms pump overlying water through their burrows (i.e., bioirrigation). In areas where groundwater discharges through sedi-

ments to the overlying water, contaminants can be carried in the advective flow either dissolved or sorbed to colloids.<sup>14</sup> An additional flux, due to molecular diffusion, occurs at the sediment-water interface, driven by the concentration gradient between sediment porewater and overlying water across a diffusion-controlled boundary layer.<sup>15</sup> Of these mechanisms, only molecular diffusion occurs in every sediment-water system. For this reason, it can be considered a conservative baseline for total flux. In addition, the gradient, which drives diffusive mass-transfer, may also be used to calculate the scale of other flux mechanisms such as bioirrigation and resuspension/desorption.

One remedial alternative that has been explored for the PVS is capping the most contaminated sediments (those near station 8C and the outfall) with a clean layer of sand. It is believed that this would have the effect of reducing contaminant flux during resuspension events as well as reducing flux due to bioirrigation by relocating benthic organisms to a cleaner sediment layer. In 2000, three 45-acre pilot sand caps (covering <0.5% of the contaminated sediment area) were installed on the PVS in

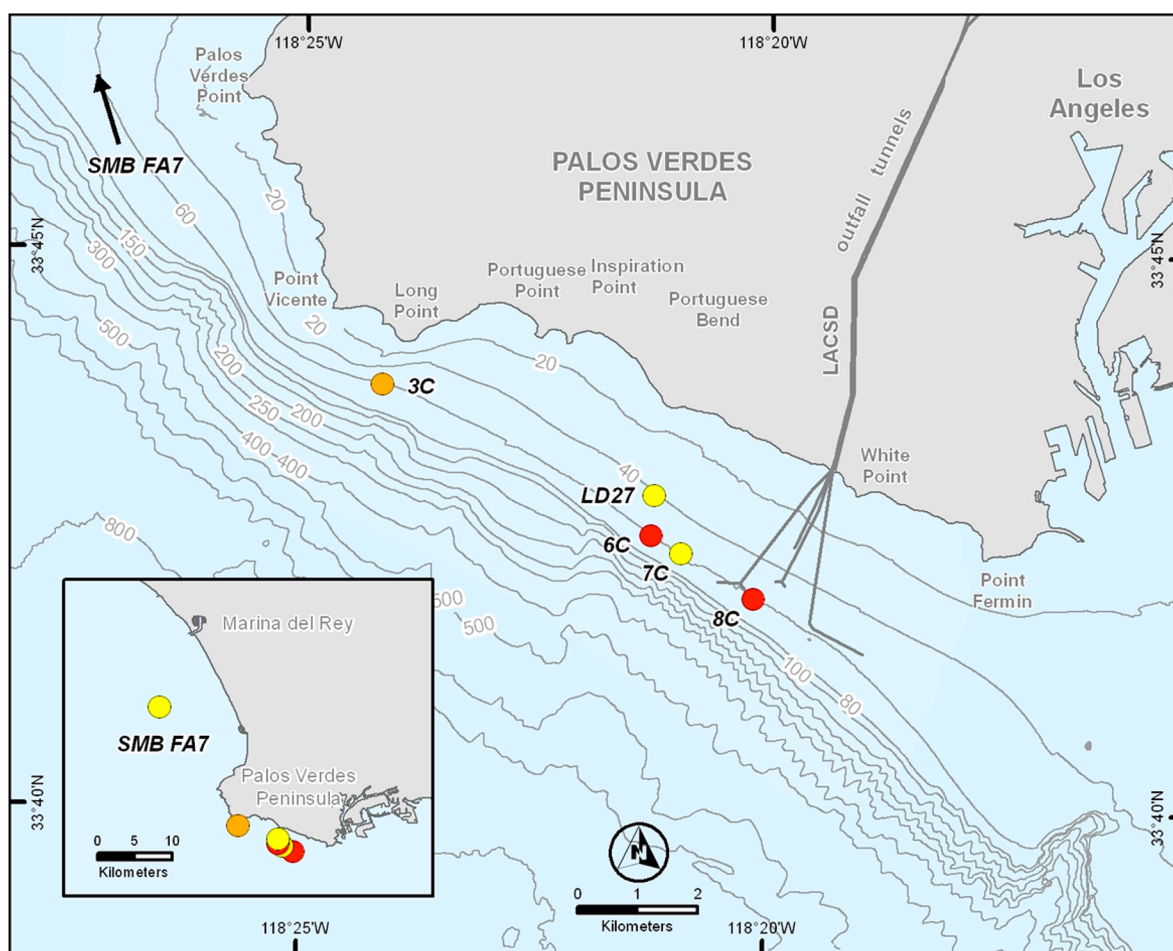
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**Figure 1.** Station locations for sediment sampling and/or passive sampler platform deployments off the coast of Los Angeles, California, USA. Lines indicate depth, with stations 8C, 7C, 6C, and 3C located along the 60 m isobath and station LD27 on the 40 m isobath. The prevailing coastal currents and wave activity carry remnants of the discharge in a northwesterly direction from the outfall, located off White Point. Sediments for laboratory assessment of porewater concentrations were collected from stations 3C, 6C, and 8C (red and orange markers). Passive sampler benthic platforms carrying PE, POM, and SPME were deployed at stations SMB FA7, LD27, 6C, 7C, and 8C (red and yellow markers). Station LD27 is located within an area where a pilot sand cap was placed in 2000. Station SMB FA7 is outside and down-current of the PVS Superfund site. Station names reflect those used in previous monitoring of sediment and water.

order to test cap placement techniques and economic feasibility. Subsequent water sampling found comparable dissolved concentrations of POPs above capped and uncapped areas.<sup>7</sup> Because advection from up-current areas along the shelf is likely, water sampling is insufficient to determine the efficacy of the caps in limiting flux of contaminants from the sediment beds to the water column. Simultaneous measurement of porewater and overlying water concentrations, however, would allow for the assessment of fluxes due to concentration gradients. By comparing measurements made within the pilot cap to those made at uncapped stations nearby, the effectiveness of the sand caps could be assessed.

Flux due to molecular diffusion of contaminants across the sediment-water surface ( $F$ ) is calculated using Fick's first law of diffusion

$$F = -\frac{D_W}{\delta_{BL}}(C_W - C_{PW}) \quad (1)$$

where  $D_W$  is the compound's diffusivity in water,  $\delta_{BL}$  is the boundary layer thickness,  $C_W$  is the concentration in the water column,  $C_{PW}$  is the porewater concentration at the surface of the sediment bed, and positive  $F$  indicates flux from sediments

to water. Using this equation and porewater concentrations estimated from sediment concentrations and an equilibrium partitioning model (EqP), Sherwood et al.<sup>16</sup> calculated diffusive fluxes of  $p,p'$ -DDE (the most abundant compound in PVS sediments) at PVS station 6C (Figure 1) ranging from 7,000 to 12,000 ng cm<sup>-2</sup> y<sup>-1</sup>. The EqP model used to estimate porewater concentration employed a sediment-water partition coefficient that considers partitioning to a single organic carbon pool. Many recent studies have shown, however, that estimating sediment-water partitioning using only organic carbon can be inaccurate, either because organic carbon–water partitioning coefficients can vary over a large range (e.g., over 2 orders of magnitude),<sup>17</sup> or because other sorptive fractions (e.g., black carbon) are included in the organic carbon fraction measurement.<sup>18</sup> Thus, calculations of  $F$  based on porewater concentrations estimated using these models could be off by orders of magnitude. In addition, concentrations in the water column have been observed to increase with proximity to the sediment surface.<sup>12</sup> Because flux calculations are based on concentrations on either side of a very thin diffusive boundary layer (tens to hundreds of  $\mu$ m thick<sup>19</sup>), measuring water

concentrations as close to the sediment-water interface as possible would improve the accuracy of calculations.

As alternatives to calculating porewater concentrations using EqP models, passive samplers, including polyethylene (PE), polyoxymethylene (POM), and solid-phase microextraction fibers (SPME), have been used to measure both water<sup>12,20–24</sup> and porewater<sup>25–30</sup> concentrations. In a related investigation, Eek et al.<sup>15</sup> used passive sampling techniques to calculate diffusive flux by equilibrating polymers with sediment slurries in the laboratory to find  $C_{PW}$ . In the current work, a different approach was taken. By deploying PE and POM strips simultaneously, in situ, across the sediment-water interface,<sup>26</sup> and using performance reference compounds (PRCs) to account for disequilibrium between the sampler and water or porewater,<sup>12,20,25,26</sup>  $C_W$  and  $C_{PW}$  bounding the diffusive layer were deduced, making flux calculations more accurate. SPME fibers, without PRCs, were also deployed to both sediment beds and overlying water for the purpose of comparing sampler results.

While the primary goal of this work was to investigate the effects of a sand cap on the flux of POPs from the sediment to the water column, the design of the newly developed benthic deployment platform allowed additional objectives to be addressed. These objectives included the following:

- (1) observe dissolved POP porewater concentrations as a function of depth at sites with and without a sand cap,
- (2) use passive sampler derived concentration gradients to calculate and compare diffusive flux of contaminants between the sediments and water column at stations with and without caps, and
- (3) compare the performance of different types of polymeric passive samplers (i.e., PE, POM, SPME) deployed together in situ.

Four stations within the PVS Superfund site were selected (Figure 1). It is expected that the direction of contaminant at these stations would be from the sediment bed to water column. One of these stations (LD27) was within a pilot sand cap area. By comparing fluxes of contaminants at the station within the pilot cap to those at nearby uncapped stations, the effectiveness of the cap in reducing diffusive flux could be assessed. A fifth station (SMB FA7) outside, and down-current, of the PVS Superfund site was included in order to determine the direction of flux at an offsite, less-contaminated station.

## MATERIALS AND METHODS

**Chemicals.** All solvents were Baker Ultraresi-analyzed (Philipsburg, NJ, USA). Laboratory water was treated with an ion-exchange and activated carbon system (Aries Vaponics, Rockland, MA, USA) until 18 MOhm-cm resistance was achieved, followed by UV exposure (TOC reduction unit, Aquafine Corporation, Valencia, CA, USA). DDTs and their breakdown products will be jointly referred to as DDX for the remainder of this work. DDX and PCB standards were purchased from Ultra Scientific (North Kingston, RI, USA) in acetone or methanol. <sup>13</sup>C-labeled PRCs and internal standards were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) in nonane.

**PE, POM, and SPME Samplers.** PE strips (10 cm × 50 cm) were prepared from low-density polyethylene sheets (25 μm thick, ACE Hardware Corp., Oak Brook, IL, USA). POM strips (10 cm × 50 cm) were prepared from polyoxymethylene sheets (76 μm thick, CS Hyde Company, Lake Villa, IL, USA). All polymer strips were cleaned and pre-equilibrated with PRCs

as described in previous work.<sup>25,26</sup> Briefly, strips were cleaned by soaking twice, for 24 h, in dichloromethane, followed by soaking twice, for 24 h, in methanol, followed by soaking twice for 24 h in water. Samplers were then soaked in water containing seven PRCs (<sup>13</sup>C labeled- p,p'-DDT, -p,p'-DDE, -p,p'-DDD, -2,4,4'-trichlorobiphenyl (PCB28), -2,2',5,5'-tetrachlorobiphenyl (PCB52), -2,3',4,4',5-pentachlorobiphenyl (PCB118), and -2,2',3,3',4,4'-hexachlorobiphenyl (PCB128)) and equilibrated for three months before deployment.

SPME fibers (100-μm PDMS coated silica fiber, Supelco, Bellefonte, PA, USA) were also prepared as previously described.<sup>12,22,29</sup> Briefly, newly purchased SPME fibers were preconditioned at 250 °C for 0.5 h prior to assembly into individual perforated copper casings for protection during deployment. Each fiber/casing assembly was kept in a sealed glass vial in a freezer at −20 °C and shipped on ice until deployment.

**Ex Situ PRC Method Testing.** While the PRC method to determine fractional equilibration ( $f_{eq}$ ) of PE samplers in sediments has been tested using deuterium labeled polycyclic aromatic hydrocarbons in the past,<sup>25,26</sup> a preliminary test using <sup>13</sup>C-labeled DDX and PCB compounds was conducted in the laboratory. The details of these tests and their results are available in the Supporting Information.

**Field Deployment and Retrieval.** Deployment platforms were designed and built to carry triplicate PE and POM samplers, and duplicate SPME samplers, to the sediment bed, allowing samplers to penetrate sediments to depths of up to 20 cm (Figures SI1 and SI2). Portions of each PE and POM sampler remained exposed to the water column, and two additional SPME fibers were positioned approximately 70 cm above the sediment-water interface. Platform bases were constructed of stainless steel, while aluminum frames holding PE and POM were secured using PVC spacers, washers, and steel bolts. Platforms were deployed from the sea surface and lowered into position above the seafloor by cable and then released. Each platform carried lead ballast to promote penetration of sampler frames into the sediment bed. Retrieval systems, consisting of a buoy, line, and acoustic release mechanism were attached to the upper portion of each platform. Using these platforms, PE and POM samplers were deployed across the sediment-water interface in triplicate (PE and POM) or duplicate (SPME), at five stations, between July 25 and 27, 2011 (Figure 1). A remotely operated vehicle (ROV), controlled by a team from the LACSD, was used to confirm proper placement of the deployment platform at each station (Figure SI3).

Platforms were retrieved from the sediments following 43 to 44 d deployments, where deployment times were selected based on modeled time required for measurable mass exchange between sampler and sediment, and the availability of the research vessel. Polymer strips were immediately cut from their frames, while marking the location of the sediment water interface (Figure SI4). Copper casings containing the SPME fibers were removed from the platforms, quickly rinsed with seawater, placed into clean capped glass vials, transferred to SCCWRP (Costa Mesa, CA, USA) on ice the same day as the recovery, and stored at −4 °C in the dark until analyzed. Field blanks (PRC loaded, unexposed samplers) were held in the air for approximately 5 min at each station to replicate the time samplers were exposed to air during deployment and recovery. Samplers and field blanks were placed in foil envelopes, stored on ice for overnight shipment to the Gschwend Laboratory



(Massachusetts Institute of Technology, Cambridge, MA, USA), and then stored in a freezer ( $-4\text{ }^{\circ}\text{C}$ ) in the dark until sectioned and extracted.

**Sampler Analysis.** PE and POM samplers were water rinsed, patted dry using Kim-wipe tissues (Kimberly-Clark Corp., Irving, TX, USA), and sectioned in the laboratory. The top of each sampler, exposed to the water above the sediment bed, was cut into two sections (10 to 18 cm in length, depending on the depth of penetration into the sediment bed). Sediment exposed portions of each sampler were cut in 1 to 2 cm sections using a razor blade and an aluminum sheet as a straight-edge. Internal (surrogate) standards (100 ng each of  $^{13}\text{C}$  labeled-*o,p'*-DDE, -2,4'-dichlorobiphenyl (PCB8), -3,3',4,4'-tetrachlorobiphenyl (PCB77), and -2,2',4,4',5,5'-hexachlorobiphenyl (PCB153)) were added to each section before extracting three times in 15 to 200 mL of dichloromethane. Combined extracts were reduced in volume using a rotary evaporator (Buchi Rotavapor-R, Brinkman Instruments, Westbury, NY, USA) and concentrated to a final volume of approximately 1 mL under a gentle stream of ultra pure grade nitrogen (Airgas, Chicago, IL, USA). Injection standard ( $d_{12}$ -chrysene) was added to each extract before final analysis.

All extracts were analyzed using gas chromatography–mass spectrometry (GCMS, JEOL GCmate, JEOL Ltd., Tokyo, Japan). On column injections ( $1\text{ }\mu\text{L}$ ) were made onto a 30 m J&W Scientific DB-XLB capillary column (0.32 mm internal diameter with a  $0.25\text{ }\mu\text{m}$  film thickness, Agilent Technologies, Santa Clara, CA, USA). The injector port temperature was initially set at  $35\text{ }^{\circ}\text{C}$  and then increased with oven temperature at a rate of  $25\text{ }^{\circ}\text{C min}^{-1}$  until  $200\text{ }^{\circ}\text{C}$  was reached. The temperature was then increased at  $4\text{ }^{\circ}\text{C min}^{-1}$  until a temperature of  $275\text{ }^{\circ}\text{C}$  was reached and held for 8 min. The MS was operated in selected ion monitoring (SIM) and EI+ modes. Calibration standards containing all target compounds (Table 1), PRCs, and internal and injection standards were run every 4 to 9 sample measurements to monitor instrument stability, determine response factors, and confirm that measurements remained within the linear range for the instrument. Using a thermal desorption extraction system, SPME fibers were manually injected on an Agilent 7890 GC/EI-MS system (Agilent Technologies, Santa Clara, CA, USA). Five-point external standard calibration curves were used to quantify the compounds.<sup>12</sup>

**Partition Coefficients.** Polyethylene-water partition coefficients,  $K_{PEW}$ , were taken from a log  $K_{OW}$  vs log  $K_{PEW}$  relationship used in previous work<sup>12</sup> and following Lohmann and Muir.<sup>31</sup> Polyoxymethylene-water partition coefficients ( $K_{POM-W}$ ) were taken from Endo et al.<sup>32</sup> Both were corrected for temperature and salinity following Lohmann<sup>33</sup> (Table 1).

**Calculation of Dissolved Concentrations.** For equilibrium passive sampling (i.e., field-deployed SPME and PE mixed with sediment slurries in the laboratory (see the SI)), water column and porewater concentrations were calculated from the mass of POP taken up by the sampler. SPME-water partition coefficients,  $K_f$  ( $L_W/L_{PDMS}$ ), were used to calculate  $C_W$  ( $\text{ng L}^{-1}$ ) from the mass of analyte sorbed to the fiber,  $N_f$  (ng)

$$C_W = \frac{N_f}{(K_f V_f)} \quad (2)$$

where  $V_f$  ( $L_{PDMS}$ ) is the volume of the sorptive polydimethylsiloxane (PDMS) coating.

**Table 1. Compounds Measured in This Study with Octanol-Water ( $K_{OW}$ ) (L/L), Polyethylene-Water ( $K_{PEW}$ ) (L/kg), and Polyoxymethylene-Water ( $K_{POM-W}$ ) (L/kg) Partition Coefficients**

compound	$K_{OW}^a$	$\log_b K_{PEW}$	T and salinity corrected log $K_{PEW}^c$	$\log K_{POM-W}^d$	T and salinity corrected log $K_{POM-W}^e$
<i>o,p'</i> -DDE		5.46	5.76	5.16	5.46
<i>p,p'</i> -DDMU	5.5 <sup>e</sup>	5.26	5.56	4.96	5.26
<i>p,p'</i> -DDE	5.7 <sup>f</sup>	5.46	5.76	5.16	5.46
<i>o,p'</i> -DDD		5.26	5.56	4.96	5.26
<i>o,p'</i> -DDT		5.93	6.23	5.65	5.95
<i>p,p'</i> -DDD	5.5 <sup>g</sup>	5.26	5.56	4.96	5.26
<i>p,p'</i> -DDT	6.19 <sup>g</sup>	5.93	6.23	5.65	5.95
PCB8	5.07	4.85	5.15	4.52	4.82
PCB18	5.24	5.01	5.31	4.69	4.99
PCB28	5.67	5.43	5.73	5.13	5.43
PCB52	5.84	5.59	5.89	5.30	5.60
PCB44	5.75	5.51	5.81	5.21	5.51
PCB66	6.2	5.94	6.24	5.66	5.96
PCB77	6.36	6.10	6.40	5.82	6.12
PCB101	6.38	6.12	6.42	5.84	6.14
PCB118	6.74	6.46	6.76	6.21	6.51
PCB105	6.65	6.38	6.68	6.12	6.42
PCB126	6.89	6.61	6.91	6.36	6.66
PCB153	6.92	6.64	6.94	6.39	6.69
PCB138	6.83	6.55	6.85	6.30	6.60
PCB128	6.74	6.46	6.76	6.21	6.51
PCB187	7.17	6.88	7.18	6.64	6.94
PCB180	7.36	7.07	7.37	6.83	7.13
PCB170	7.27	6.98	7.28	6.74	7.04
PCB195	7.56	7.26	7.56	7.04	7.34
PCB206	8.09	7.77	8.07	7.57	7.87
PCB209	8.18	7.86	8.16	7.66	7.96

<sup>a</sup>log  $K_{OW}$  for PCBs from Hawker and Connell.<sup>35</sup> <sup>b</sup>25  $^{\circ}\text{C}$ , no salt.<sup>12</sup> <sup>c</sup>12  $^{\circ}\text{C}$ , 0.5 M salt. <sup>d</sup>Endo et al.<sup>32</sup> <sup>e</sup>EPISuite estimate.<sup>36</sup> <sup>f</sup>Pontolillo and Eganhouse.<sup>37</sup> <sup>g</sup>Schwarzenbach et al.<sup>38</sup>

For nonequilibrium sampling (i.e., PE inserted to jars in laboratory (see the SI), and PE and POM strips exposed in the field), PRC and target compound concentrations in PE and POM sampler sections were used to calculate dissolved concentrations of target compound in the water column and pore waters<sup>12,25,26</sup>

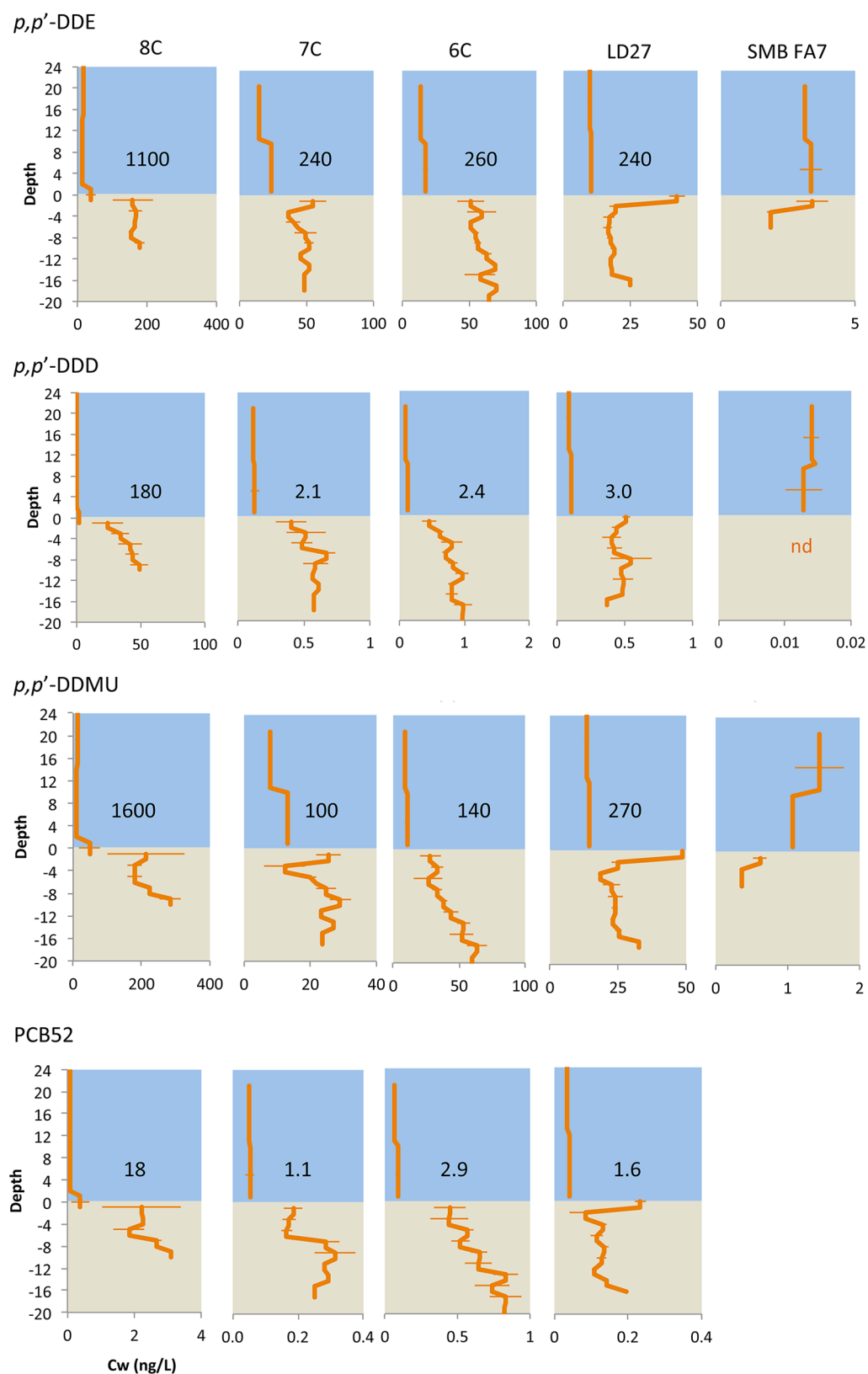
$$C_W = \frac{C_{polymer}^{\infty}}{K_{Polymer-W}} \quad (3)$$

$$C_{polymer}^{\infty} = \frac{C_{polymer,t}}{f_{eq}} \quad (4)$$

and

$$f_{eq} = \frac{(C_{PRC}^0 - C_{PRC,t})}{C_{PRC}^0} \quad (5)$$

where  $C_{polymer}^{\infty}$  is the equilibrium analyte concentration in the PE or POM in  $\text{ng kg}^{-1}$ ,  $K_{Polymer-W}$  is the compound-specific polymer–water partition coefficient ( $K_{PEW}$  or  $K_{POMW}$  ( $\text{L kg}^{-1}$ )),  $C_{polymer,t}$  is the concentration in the PE or POM after deployment,  $C_{PRC}^0$  is the initial concentration of PRC in the sampler,  $C_{PRC,t}$  is the concentration of PRC in the sampler after



**Figure 2.** Water column and porewater concentration profiles with depth of  $p,p'$ -DDE,  $p,p'$ -DDD,  $p,p'$ -DDMU, and PCB52 at each station. Values are the average of those generated using three PE passive samplers. Error bars reflect standard error. Values in black are the calculated flux from sediment porewater to the water column in  $\text{ng cm}^{-2} \text{y}^{-1}$ . PCB52 was not detected in the porewaters at the SMB station. Blue background indicates water column matrix and beige background indicates sediment matrix. The  $x$ -axis scales are different for each station and compound to improve resolution of vertical trends.

deployment, and  $f_{eq}$  is the fractional equilibration of the POPs between the sampler and water. Polymer–water partition coefficients (Table 1) were corrected for the temperature and salinity previously observed in the waters and sediments of PVS<sup>34</sup> following methods described by Lohmann.<sup>33</sup>

The  $f_{eq}$  of the  $^{13}\text{C}$ -labeled  $p,p'$ -congeners of DDX compounds were used to determine the fraction equilibration for both  $p,p'$ - and  $o,p'$ -forms of the target compounds. The  $f_{eq}$ s of  $^{13}\text{C}$ -PCB28,  $^{13}\text{C}$ -PCB52,  $^{13}\text{C}$ -PCB118, and  $^{13}\text{C}$ -PCB128 were used as the  $f_{eq}$ s for di- and trichlorobiphenyl (PCB8, -18, and -28), tetrachlorobiphenyl (PCB52, -44, and -66), pentachlorobiphenyl (PCB101, -118, and -105), and hexa- and septachlorobiphenyl (PCB153, -138, -128, -187, -180, and -170) target compounds, respectively.

DDX and PCB concentration data from the water column and porewater at the sediment surface of each station were used to calculate diffusive flux for several compounds using eq 1. A boundary layer thicknesses,  $\delta_{BL}$ , of 0.02 cm was used for all compounds and all stations based on calculations following Sherwood et al.<sup>16</sup> and Chen<sup>19</sup> (kinematic viscosity of  $0.013\text{ cm}^2\text{ s}^{-1}$  and friction velocity of  $0.5\text{ cm s}^{-1}$  were used to calculate  $\delta_{BL}$ ).

## RESULTS

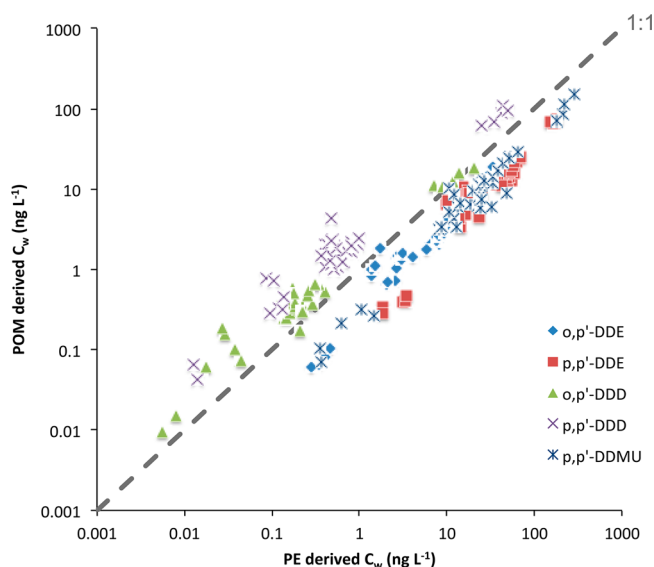
Fractional equilibration of PRCs in field exposed samplers varied by compound, sampler type, and environmental matrix (Tables SI1 and SI2). Except for DDT,  $f_{eq}$  tended to decrease with increasing polymer–water partition coefficient within each class of compound.  $^{13}\text{C}$ -labeled DDT was more depleted in PE exposed to sediments than expected. In most cases, there was better agreement among PE samplers than POM samplers in terms of  $f_{eq}$ . Slightly greater  $f_{eq}$  were observed in water-side samplers than in sediment side samplers for the more water-soluble compounds, while the trend reversed for the less soluble, penta- and hexachlorobiphenyls.

Water and porewater concentrations were calculated using data from three types of passive samplers for DDXs and PCBs. Water concentrations from PE and POM reflect integrated values over two sections (0 to 10–15 cm above the sediment–water interface, and 10–15 to 20–30 cm above the interface), while SPME sampled water approximately 70 cm above the interface. Porewater concentrations from PE and POM reflect integrations over 1 to 2 cm intervals, to a maximum depth of 20 cm (Tables SI3 and SI4 and Figure 2), while SPME generated porewater concentrations reflect integrations over a 10 cm window at depths between 0 and 20 cm depending on the station. In each set of data, the contaminant observed at the highest concentrations at every station, in either the water column or porewater, was  $p,p'$ -DDE. Using PE generated concentrations,  $p,p'$ -DDE averaged  $86 (\pm 6)\%$  of the total combined DDX concentrations. The PCBs observed at the highest concentrations were the tri- and tetrachlorobiphenyls, PCB18, -28, -44, and -52, in the range of nanograms per liter in the porewaters at station 8C. Larger PCBs, such as hexa- and septachlorobiphenyls (PCB128, 138, 153, -180 and -187) were calculated to be in the range of 3 to  $110\text{ pg L}^{-1}$  in the porewater at the same station but below detection limits ( $1$  to  $40\text{ pg L}^{-1}$  for these PCBs) at other stations.

POP concentrations measured just above the sediments at each station were about ten times greater than those measured 5 m above the sediment–water interface a year earlier.<sup>12</sup> This is consistent with observations of increasing dissolved concentrations with depth in the water column. Also, dissolved DDE

concentrations just above the sediments are 2 to 5 orders of magnitude greater than background concentrations calculated from measurements in floating PE debris collected from the Northern Pacific Gyre.<sup>39</sup>

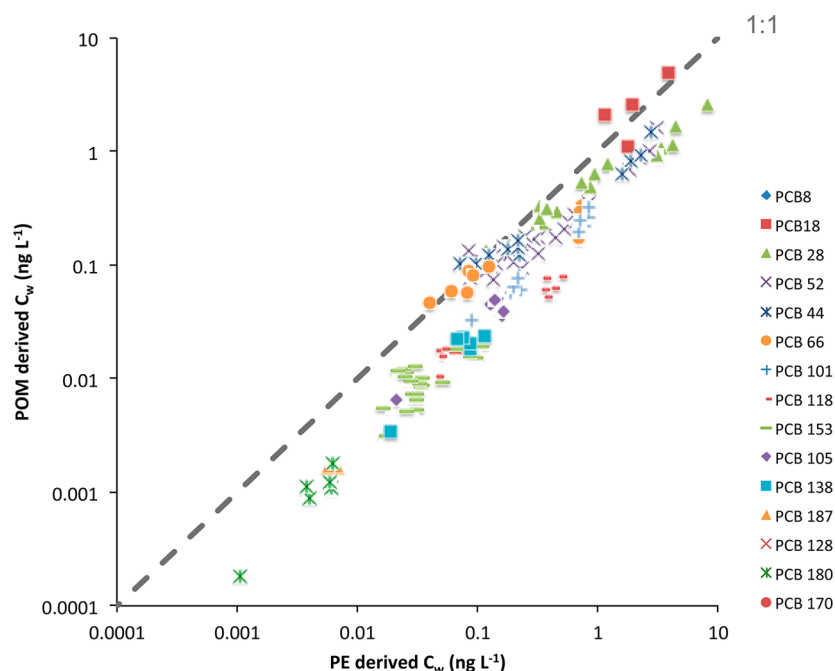
**Field-Deployed Sampler Comparisons.** In general, dissolved POP concentrations determined using PE and POM agreed within 1 order of magnitude. Given uncertainties of 0.2 to 0.5 log units reported for measured and estimated partition coefficients,<sup>20,32,33</sup> agreement within only an order of magnitude is not surprising. More specifically, concentrations of DDXs measured using the two samplers agreed within a factor of 5, with  $p,p'$ -DDD showing the closest agreement (Figure 3).



**Figure 3.** Water column and porewater concentrations generated using field-deployed (in situ) POM and PE samplers for DDX compounds. Dashed line indicates 1:1 agreement between values.

Dissolved concentrations of DDEs and DDMU generated from PE measurements were always greater than those generated from POM, while dissolved concentrations of DDDs generated from PE measurement were most often lower than those generated from POM. PE generated PCB concentrations were most often greater than those generated from POM data, with the greatest divergence seen in the septachlorobiphenyl PCB180 (Figure 4). These general trends for differences in calculated water concentrations, for specific compounds, using the two sampler materials, are expected where partition coefficients are uncertain as described above.

Because SPME samplers were exposed to water almost a meter above the sediment–water interface, direct comparison of resulting dissolved concentrations to those resulting from PE and POM samplers, exposed within 20 cm of the interface, is not reasonable. In a previous study using PE and SPME samplers in the water column at the PVS Superfund site, concentrations of DDE were observed to increase with depth.<sup>12</sup> SPME derived dissolved concentrations of  $p,p'$ -DDE measured approximately 70 cm above the sediment–water interface in this work are 2 to 5 times greater at stations 7C and 8C than those measured using SPME suspended 5 m above the sediment–water interface in 2010. These measurements would be consistent with a trend of increasing concentrations with approach to sediment bed.



**Figure 4.** Water column and porewater concentrations generated using field deployed (in situ) POM and PE samplers for selected PCBs. Dashed line indicates 1:1 agreement between values.

PE and SPME derived porewater concentrations, however, were very different. Porewater concentrations determined using PE were up to 230 times larger than those determined using SPME. This large discrepancy may have been due to the way SPME were deployed to the sediment beds. We suspect that attaching SPME copper casings inside of L-shaped steel bars did not allow for sufficient contaminant mass-transfer between porewater and the SPME fibers. As in previous work,<sup>12</sup> another reason calculated dissolved concentrations may differ between the types of samplers deployed is that PE and POM were corrected for nonequilibrium using PRCs, while SPME fibers were assumed to be fully equilibrated. No experiments were conducted, however, that would confirm that SPME deployed in this manner would have reached equilibrium with sediment porewaters within the 43 to 44 d deployment times.

## DISCUSSION

**Laboratory versus Field Measurements.** As previously observed for sediments containing polycyclic aromatic hydrocarbons,<sup>25,26</sup> the experiments conducted in the laboratory using field-collected sediments confirmed that the method of using PRCs to account for disequilibrium between PE and water or porewater is effective (Figures SI5, SI6, and SI7). In addition, laboratory and field exposed PE samplers yielded similar results. Porewater concentrations of *p,p'*-DDE measured using PE (with PRCs) in the laboratory were 170 and 84 ng L<sup>-1</sup> at stations 8C and 6C, respectively, while porewater concentrations measured in the surface sediments following in situ PE deployment were 160 and 51 ng L<sup>-1</sup> at stations 8C and 6C, respectively. Similar agreement was seen for *o,p'*-DDE and *p,p'*-DDMU in the same samples.

**POP Flux between Sediments and Water Column.** While the passive sampling methods used in this work could not resolve the dissolved concentrations at the same scale as the calculated diffusive boundary layer (100 μm scale), the concentrations could be measured much closer to those

boundaries than have been attempted in the past (cm scales). Also, because passive samplers are time integrative, temporal variability in water concentrations advecting past each station could not be detected. Concentrations near the sediment-water interface at the PVS stations were assumed to be constant for the calculation of diffusive flux. As expected, the station with the highest previously measured sediment concentrations (8C)<sup>40</sup> was calculated to have the greatest flux of POPs from sediment to water column (Figure 2 and Table 2). Calculated fluxes for DDX were similar at each of the other stations on the PVS (7C, 6C, and LD27). At the off-site station (SMB FA7), fluxes were too small to calculate (concentrations in water and porewater were the same within uncertainty).

The diffusive flux at station 6C calculated using the data collected for this work was more than an order of magnitude

**Table 2.** Calculated Flux in ng cm<sup>-2</sup> y<sup>-1</sup> for DDX and Selected PCB Congeners Calculated from PE Sampler Results<sup>a</sup>

compound	station			
	8C	7C	6C	LD27
<i>o,p'</i> -DDE	190 (±90)	42 (±19)	43 (±22)	33 (±5)
<i>p,p'</i> -DDMU	1600 (±300)	100 (±66)	140 (±90)	270 (±10)
<i>p,p'</i> -DDE	1100 (±300)	240 (±150)	260 (±140)	240 (±40)
<i>o,p'</i> -DDD	52 (±30)	0.71 (±0.46)	1.4 (±0.4)	0.88 (±0.27)
<i>p,p'</i> -DDD	180 (±70)	2.1 (±1.6)	2.4 (±1.5)	3.0 (±0.4)
PCB28	28 (±5)	1.7 (±0.4)		
PCB52	18 (±1)	1.1 (±0.4)	2.9 (±1.6)	1.6 (±0.2)
PCB101	5.9 (±1.1)	0.62 (±0.35)	0.68 (±0.40)	0.78 (±0.18)
PCB153	0.7 (±0.2)		0.14 (±0.05)	0.25 (±0.03)

<sup>a</sup>Positive values indicated flux from sediment porewater to water column. Blank values indicate no flux could be calculated because gradient was within uncertainty. Uncertainty calculated from propagation of error (1 SD, *n* = 3) of dissolved concentrations in porewater and bottom water.



lower than that calculated by Sherwood et al.<sup>16</sup> using porewater concentrations estimated from sediment concentrations and organic carbon fractions. Considering the assumptions of the EqP model used in the Sherwood et al. estimate, this is not surprising. Because the same EqP model was used in their work to calculate desorption during resuspension events, the modeled flux due to resuspension events may also be proportionally off. Even if a field campaign for making in situ measurements as described here is not viable, determining dissolved concentrations using passive samplers exposed to bulk sediment in the laboratory could improve calculations of site-specific sediment-water partition coefficients,  $K_d$ , used in the calculation of fluxes due to molecular diffusion and resuspension/desorption.

**Sediment Porewater Concentration Gradients.** While only the surface sediment porewater concentrations (0–2 cm) were used in calculating diffusive flux of POPs between sediment and water, porewater concentrations profiles with depths were collected (Figure 2). Although the highest sediment concentrations observed in cored samples from stations 8C, 7C, and 6C were found at depths of 20 to 42 cm (U.S. EPA, unpublished data), samplers in this work only reached a maximum depth of 20 cm. Slight gradients with depth may be observed for DDD and DDMU at the uncapped PVS stations, while DDE concentrations appear to be more uniform within the top 20 cm of sediments. The capped site (LD27) shows sharply higher concentrations of DDE, DDMU, and PCB in the top sediment section (0–2 cm depth) similar to those observed at nearby station 6C, while the deeper porewaters had about half the concentration observed at station 6C. While a layer of higher concentration may have formed as sediment, disturbed during the cap placement, resettled, it may also have been generated by sediments from another location settling following resuspension events since cap placement. The second alternative is more consistent with observations made during monitoring of the capped area. While the cap depth at this station is expected to be between 4 and 16 cm,<sup>41</sup> it is not possible to determine if the sampler crossed the sand cap into the original sediment bed.

**Effects of the Sand Cap on Flux.** Flux calculations based on concentration gradients between the surface sediment layer and the water column above the sediments indicate that the exchange of POPs between sediment and water in the sand capped area due to molecular diffusion is similar to that at nearby stations (Figure 2 and Table 2) ( $240 \text{ ng cm}^{-2} \text{ y}^{-1}$  at station LD27 vs  $260 \text{ ng cm}^{-2} \text{ y}^{-1}$  at station 6C). Assuming that the porewater concentrations at this station are representative of the capped area, the sediments in the capped zone continue to be a source of contamination to the water column in terms of diffusive flux. If the surface layer of sediments with relatively higher porewater concentrations of DDE, DDMU, and PCBs were not present (i.e., surface porewater concentrations were those measured below 2 cm depth in sediments), it could be assumed that the diffusive flux at the station would be reduced by about one-half.

While we did not directly investigate the effects of the sand cap on desorption during resuspension events or on the tissue concentrations of benthic organisms, the porewater concentration data can inform estimates of those effects. Porewater concentrations in the sediment surface layer indicate the maximum concentration the water in contact with resuspended particles would reach. These data can be combined with desorption kinetics models to refine calculations of flux due to

resuspension events. Also, tissue concentrations of benthic organisms have been shown to correlate with dissolved porewater concentrations.<sup>42</sup> Depending on the sediment horizon with which benthic organisms in the capped area are most associated, and assuming that sediments below the cap are like those at nearby station 6C, the cap could have the effect of lowering tissue concentrations by half (for organisms associated with sediments below 2 cm thick surface layer, but within capping material) or could have no effect (for organisms associated with sediments in the top 2 cm). Consequently, given these considerations, the cap has the potential to be an effective tool for separating contaminated sediments at PVS from the water column except that the cap itself has been “capped” by contaminated sediments, presumably from another part of the PVS or by sediments disturbed during cap placement. An effective remedy would require the cap to be placed over the most contaminated sediments, using methods that avoid resettling of sediment on cleaner cap material.

**Future Work.** Although it is expected that the qualities of organic sorbents present in the sediment bed vary across the PVS, the results of this work could contribute to the general accounting of contaminant mass into and out of the water column above the PVS. Porewater concentrations calculated in this work could be combined with bulk sediment concentrations and organic carbon fractions measured previously<sup>40</sup> to produce representative organic carbon–water partition coefficients,  $K_{OC, PVS}$  for PVS sediments. These partition coefficients combined with organic carbon fractions and POP concentrations in sediments and water column<sup>12</sup> could be used to account for shelf wide contaminant mass transfers. These types of analyses will be the subjects of continued work. In addition, passive samplers and deployment platforms, like those used in this work, could be used to investigate the efficacy of remedial efforts in sediments or to determine the magnitude of sediments as a source or sink for POPs in other aquatic systems.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Methods for ex situ PRC method testing. Results of ex situ equilibrium vs nonequilibrium (PRC) method testing. Tables of  $f_{eq}$  in PE and POM samplers. Tables of PE, POM, and SPME deduced water column and porewater DDX and PCB concentrations. Images of sampler platform design, deployment, and recovery. Figures comparing results of equilibrium and nonequilibrium sampling of sediment samples in the laboratory to TOC-corrected slurry water concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.



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